

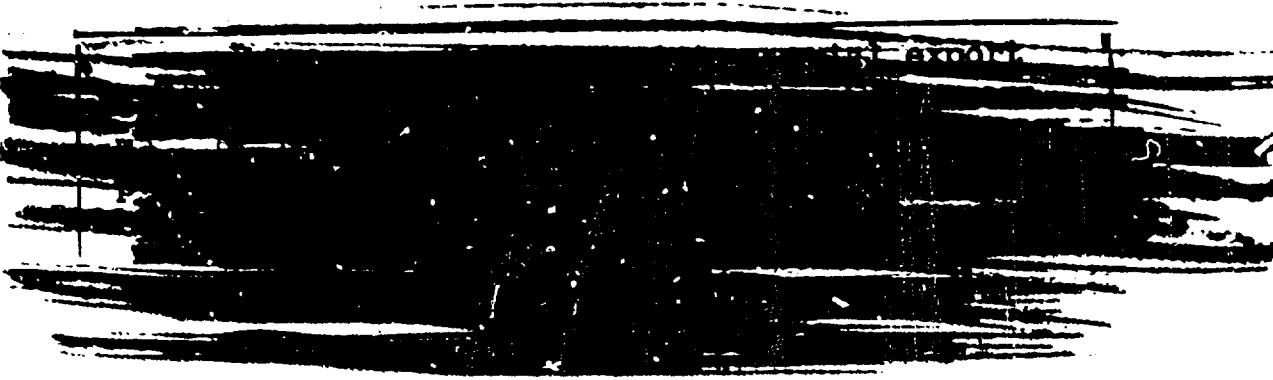
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THE PRESSURE DEPENDENCE OF THE SOLID STATE  
REACTION BETWEEN MAGNESIUM AND TEFLON

\* \* \* \* \*

Eugene O. Speckart



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by

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Submitted in partial fulfillment of  
the requirements for the degree of

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Monterey, California

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This work is accepted as fulfilling  
the thesis requirements for the degree of  
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#### ABSTRACT

The effect of low pressure on the solid state reaction between magnesium and Teflon was investigated with the percent completion of the reaction the parameter considered. A reaction mechanism and the principal products of the reaction were determined. No noticeable effect on the percent completion was observed at pressures greater than 350mm of mercury, however the percent dropped off in an exponential fashion below 350mm to a minimum at 12mm, the lowest pressure considered.

The writer wishes to express his appreciation for the assistance and encouragement given him by Professor James E. Sinclair of the U. S. Naval Postgraduate School in this investigation.

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## SYMBOLS AND ABBREVIATIONS

$V_0$  - Total volume of system

$V_s$  - Volume of acid introduced into system

$V_2$  - Measured volume of gas in buret

$T_0$  - Temperature at time of introduction of acid

$T_2$  - Temperature of gas and acid within system

$P_0$  - Pressure within system at time  $T_0$

$P_1$  - Barometric pressure at time  $T_0$

$P_2$  - Total pressure of gas and acid within system

$P_a$  - Partial pressure of air at total pressure  $P_2$

$P_3$  - Vapor pressure of water at  $T_2$

$P_n$  - Normalized partial pressure of air

$P_h$  - Partial pressure of hydrogen at total pressure  $P_2$

$P_m$  - Normalized partial pressure of hydrogen

$S_1$  - Solubility of air at  $T_0$  and  $P_1$  less vapor pressure of water

$S_2$  - Solubility of air at  $T_2$  and  $P_a$

$\Sigma N$  - Total moles of gas in buret

$N_1$  - Moles of undissolved air in buret

$N_2$  - Total moles of air in system, dissolved and undissolved

$N_3$  - Moles of dissolved air within system

$N_4$  - Solubility of air in  $V_s$  at  $T_2$  and  $P_a$

$N_5$  - Solubility of air in  $V_s$  at  $T_2$  and 760mm less vapor pressure of water

$N_6$  - Moles of undissolved hydrogen in buret

$N_7$  - Total moles of hydrogen in system, dissolved and undissolved

$N_8$  - Moles of dissolved hydrogen in system

$M_m$  - Mass of magnesium in system prior to ignition

$M_p$  - Mass of pellet prior to ignition

$M_Y$  - Mass of magnesium remaining after ignition

$C_g$  - Concentration of undissolved hydrogen at  $T_2$  and  $P_h$

$C_1$  - Concentration of dissolved hydrogen at  $T_2$  and  $P_h$

$f$  - Ratio of air dissolved in  $V_g$  to solubility in  $V_g$  at  $T_2$  and  $P_a$

$B$  - Ratio of  $C_1$  to  $C_g$

$\pi$  - Mass fraction of magnesium in mixture

$P_i$  - Pressure of inert atmosphere in which pellet was fired

$E$  - Percent completion of the reaction

UNITS

Volume Milliliters

Temperature Degrees centigrade

Pressure Millimeters of Mercury

Moles Millimoles

Solubility Millimoles per liter except as noted

Mass Milligrams

## INTRODUCTION

The reaction between solid compounds or between solid elements and compounds such as those used in propellants, boosters, and igniters is normally accelerated by an increase in the pressure of the surrounding atmosphere. An example is black powder which deflagrates when ignited in a closed container under pressure while in the open at room pressure it burns slowly. By a further reduction in pressure below atmospheric, it is conceivable that a pressure could be reached where the reaction would either not proceed at all or the extent to which it would proceed would be greatly reduced.

This pressure effect was studied using a mixture of powdered magnesium and powdered Teflon.<sup>1</sup> This system was chosen since it is non-hygroscopic, is relatively inert at room temperature and pressure both as a mixture and in single component form, and results in no gaseous products at room temperature. Systems such as lithium, zirconium, and aluminum with Teflon were considered. The lithium and zirconium systems were discarded because of the inherent difficulties in handling the pure metal in powdered form. The aluminum system was discarded due to a lack of ignition reliability at atmospheric pressure.

Small pellets consisting of a Teflon rich mixture were ignited in an inert atmosphere at various pressures ranging from approximately 700 millimeters of mercury to ten millimeters. An excess of Teflon was used to insure that the failure of any magnesium to react was due solely to the inability of the pellet to sustain burning. The quantity of unreacted

<sup>1</sup>Teflon is the trade name for polytetrafluoroethylene produced by E. I. duPont de Nemours, Inc.

magnesium and thus the extent to which the reaction proceeded was determined by introducing a dilute acid solution and measuring the volume of hydrogen resulting from the reaction between magnesium and the acid.

## BACKGROUND

The generally accepted theory for the thermal ignition and burning of igniter type solid materials is that highly reactive gases are first generated by the decomposition or vaporization of one or more of the constituents. These gases remaining in close contact with the solid surfaces are then heated to the point where they flash, initiating ignition, which then goes into steady state burning /1/. Studies conducted at Princeton University on the ignition and burning of solid propellants and igniters indicated that pressure seemed to be the most important factor in steady state burning /2/. Tests on nitrocellulose conducted in the Ballistic Research Laboratory, Aberdeen Proving Ground indicated that the heat of explosion is a function of the initial pressure of the surrounding inert atmosphere /3/.

Brair, Churchill, and Thatcher investigated the effect of the temperature of hot gases on ignition time delay /4/. Their results indicated that ignition time is related to the temperature of the generated gases by an Arrhenius type equation.

Experiments in an oven have shown that gases evolve from Teflon at a temperature of about  $425^{\circ}\text{C}$  /5/. These gases have been established to be poisonous fluorocarbons containing two, three, and four carbons however some doubt exists as to the exact structures. The three and four carbon compounds have either propene and butene or cyclopropane and cyclobutane structures, and quite possibly a mixture of both.

Coffin investigated the burning of magnesium ribbon in oxygen /6/. His results strongly indicate a vapor phase mechanism for the combustion of the magnesium ribbon. Hartman and Schneider, and Kelley have reported values for the vapor pressure of magnesium ranging from one millimeter at a temperature of  $621^{\circ}\text{C}$  to 760 millimeters at  $1107^{\circ}\text{C}$  /7 and 8/.

Preliminary tests were conducted with the Teflon to obtain an approximate temperature at which gas evolution began and on the magnesium-Teflon mixture to obtain an approximate ignition temperature. Gases evolved from the Teflon at temperatures in the range  $405^{\circ}\text{C}$  -  $420^{\circ}\text{C}$  when heated under a pressure of 500 microns. Pellets of the magnesium-Teflon mixture were ignited and proceeded to steady state burning at a temperature of approximately  $650^{\circ}\text{C}$  under atmospheric pressure. At extremely low pressure the pellets could not be ignited at this temperature.

The reacting mixture and the reaction products were examined by X-ray diffraction. Weak magnesium oxide lines were observed on the diffraction pattern of the magnesium-Teflon mixture in addition to the primary constituents. The same weak magnesium oxide lines were observed on the pattern of the products as well as very intense magnesium fluoride lines and carbon lines, however the lines originally attributed to the Teflon had completely disappeared and were replaced by lines assumed to be from lower molecular weight fluorocarbons.

## APPARATUS AND MATERIAL

The magnesium-Teflon pellets were ignited electrically in a stainless steel bomb system (Figures 1 and 2a). The volume of the bomb, 770 milliliters, was quite large compared to the size of the pellets ignited. Use of this design was primarily for the purpose of reducing to a minimum any build up of pressure during the reaction due to the hot gases formed while the reaction was in progress. A pure nickel liner was inserted in the lower portion of the bomb to eliminate any reaction with impurities in the steel since the reaction was slow enough to allow the pellet to fall to the bottom of the bomb before completion. All glass-to-glass and glass-to-metal joints were made using plain O-ring joints and ball and socket joint clamps. The metal fittings were fabricated from stainless steel with joint dimensions identical to those of the glass. The resulting glass-to-metal joints were extremely satisfactory and could be dismantled rapidly when necessary. During low pressure tests the system was maintained at a pressure of 500 microns for periods of three and four hours with no measurable change in internal pressure. The volume of the bomb and gas buret with all bomb valves closed except that leading to the buret was 830.00 milliliters. All pellet ignitions, hydrogen solubility corrections, and mass fraction of magnesium in the mixture determinations were made using this apparatus. The fitting shown in Figure 2b was used in place of the buret to determine the correction for dissolved air entering the system with the acid. The dimensions of this fitting were identical with those of the buret except for the length of the tube and the addition of the manometer at the upper end. The volume of the fitting was varied a slight amount by varying the amount of mercury in the manometer to obtain the desired pressures within the

system.

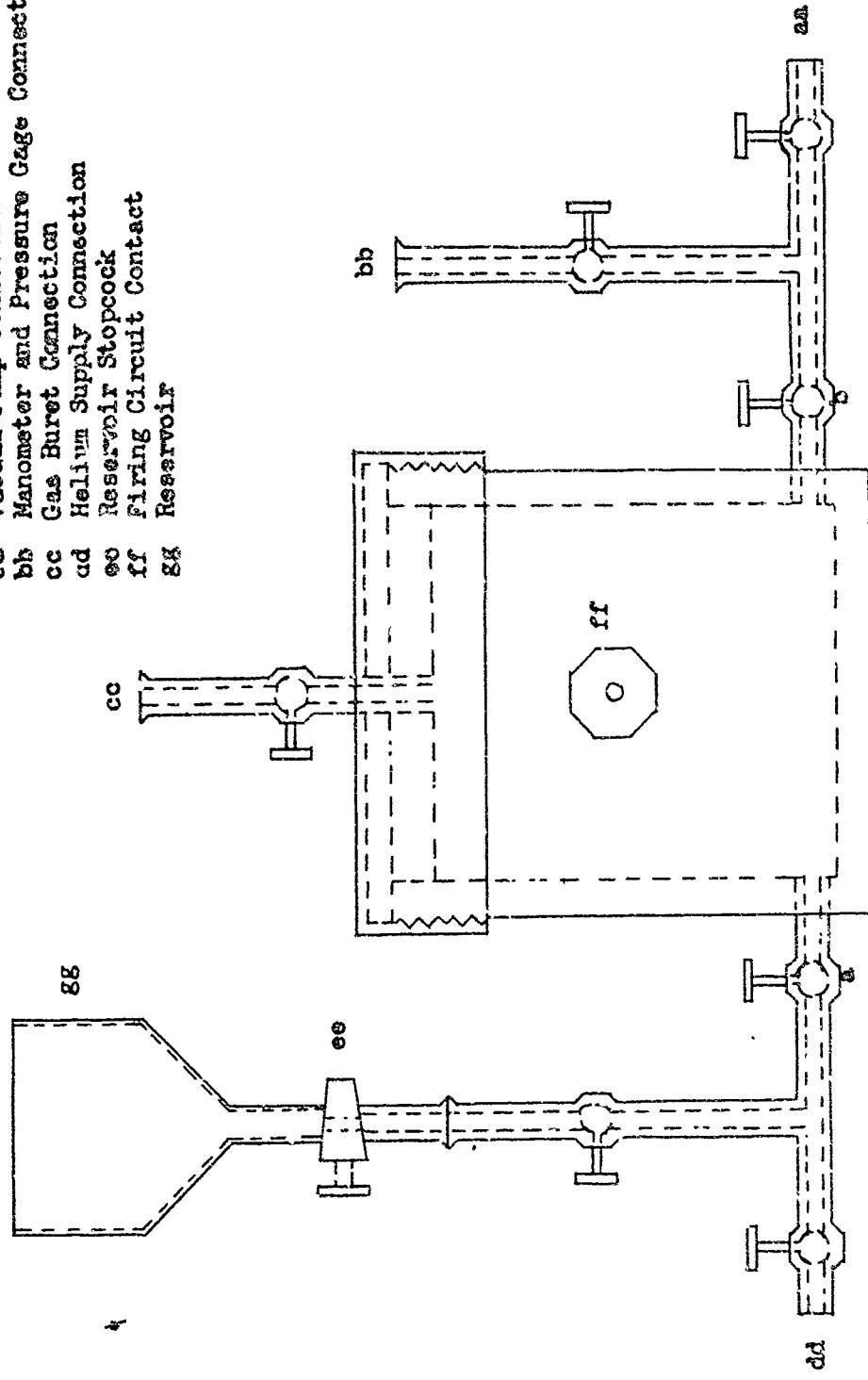
The firing circuit (Figure 3) contained an ammeter to indicate positive firing. Upon ignition of the pellet the heat of the reaction melted the ignition wire and the breaking of the circuit was indicated by the ammeter.

The magnesium-Teflon mixture was made of finely ground magnesium, mesh 325, and Teflon No. 7, a finely powdered form with particle size approximately the same as the magnesium. The magnesium was analyzed for magnesium oxide content by determining the density of a compressed pellet and by measuring the volume of hydrogen evolved from the reaction of the magnesium and sulphuric acid at a partial pressure of hydrogen at which the solubility of hydrogen in the acid was negligible. The analysis of the magnesium indicated that it contained 12.9% magnesium oxide. The pellets were made by lightly compressing the mixture with a platinum wire passing through the pellet and varied in mass from approximately 15 milligrams for low pressure ignitions to 75 milligrams for higher pressure ignitions. Platinum ignition wire was used to insure that no reaction would take place between the wire and the pellet. The pellets were lightly compressed to insure that the reaction between the acid and any unreacted magnesium would take place within ten minutes. The compression pressure was sufficient to insure normal ignition and burning at atmospheric pressure. Tests of the pellets indicated that the compression pressure was sufficient to prevent blowing apart of the pellet during burning.

The acid solution used was one-tenth normal sulphuric and was prepared by diluting the standard reagent grade. For all determinations the acid was saturated with air at room temperature and pressure. Water, also

saturated with air at room temperature and pressure, was used in lieu of the acid solution once the acid-magnesium reaction was completed.

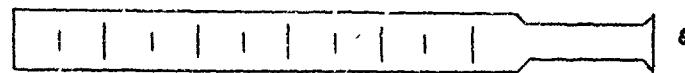
ee Vacuum Pump Connection  
 bb Manometer and Pressure Gage Connection  
 cc Gas Buret Connection  
 dd Helium Supply Connection  
 ee Reservoir Stopcock  
 ff Firing Circuit Contact  
 gg Reservoir



Bomb and Bomb Fittings

Figure 1

a Bomb Connection



Gas Buret

Figure 2a

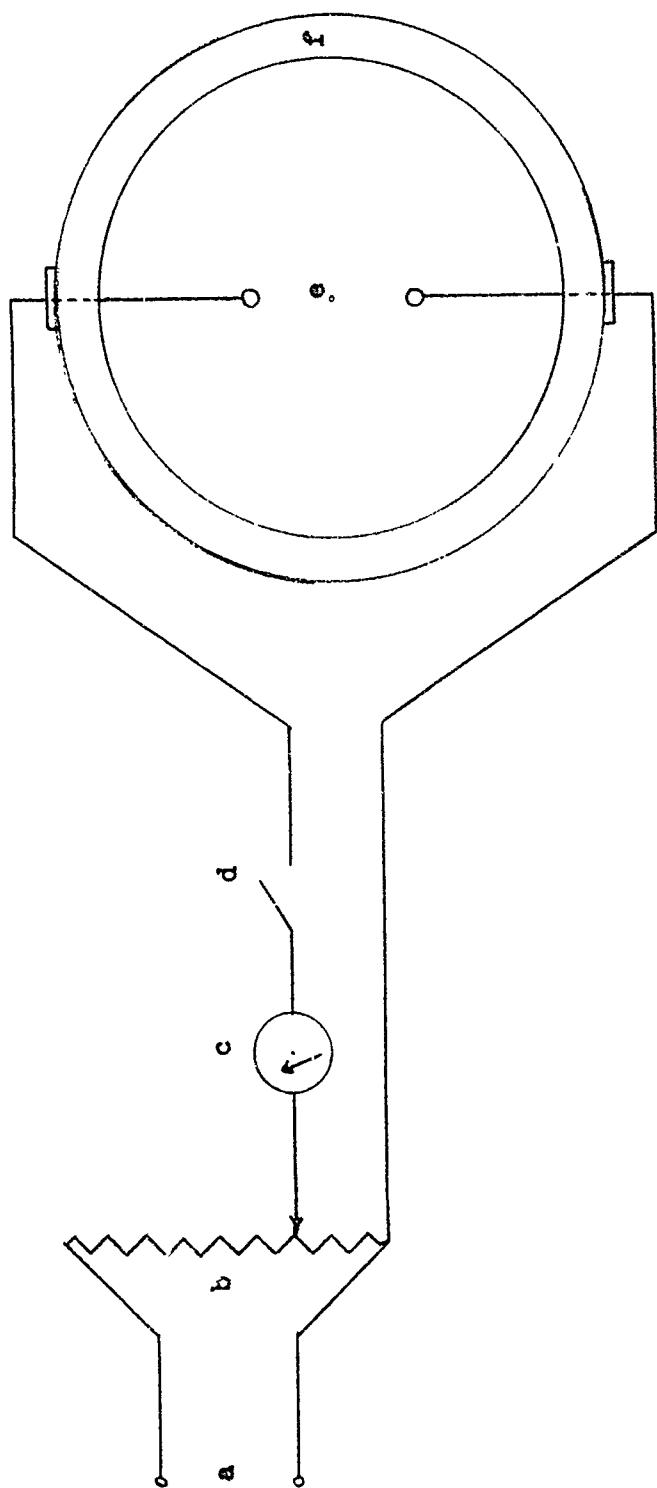
a Bomb Connection  
b Manometer Connection



Air Correction Fitting

Figure 2b

- a 110 Volt Source
- b 10 Amp Varac
- c Ammeter
- d Firing Key
- e Pellet Ignition Wire Contacts
- f Bomb Wall



Firing Circuit

Figure 3

#### PROCEDURE

Since the acid introduced into the system was saturated with air it was first necessary to determine a correction for the amount of air that would be included in the final gas volume measurement. This was done by determining the fraction of air that remained dissolved in the acid within the system. With the fitting shown in Figure 2b in place on the bomb cover fitting, the reservoir was filled with 300 milliliters of acid. All internal valves except the reservoir stopcock were opened and the system was evacuated to approximately 500 microns. Valve "a" was then closed and the reservoir stopcock opened and 257 milliliters of acid allowed to flow into the bomb. Valve "b" was then closed and the reservoir refilled with water. After a ten minute waiting period, to simulate actual test conditions, valve "b" was opened and the system was brought to the desired pressure by allowing water to flow in. Measurements were taken at various partial pressures of dry air from approximately 250 millimeters to 750 millimeters. The system was then allowed to stand until the volume of gas in the tube remained constant over a period of fifteen minutes. The volume of gas, the volume of liquid admitted, the temperature and the internal pressure were then recorded.

The hydrogen solubility correction was determined in the same manner as the air correction except that the buret was attached to the buret fitting on the bomb cover and a known mass of magnesium was placed in the bomb prior to evacuation. The concentration of hydrogen in acid was determined for partial pressures of dry hydrogen from approximately 100 millimeters to 450 millimeters. The final total pressure in the system was always room pressure and the partial pressure of hydrogen was varied by introducing varying masses of magnesium into the system.

The mass fraction of magnesium in the mixture was determined in the same manner as the hydrogen solubility correction except that known masses of the magnesium-Teflon mixture were used in lieu of magnesium.

The actual tests were conducted by attaching the pellet ignition wire to the electrical contacts, filling the reservoir with 300 milliliters of acid and evacuating the system with all valves open except valve "c" leading to the burret and the reservoir stopcock. The system was then vacuum flushed four times with helium to remove all air. The desired pressure in the system was then obtained by allowing the required amount of helium to enter. When the pressure reached a constant value within the system valves "a" and "b" were closed, the firing circuit contacts attached, and the pellet ignited. A period of five minutes was allowed after ignition was indicated to insure that the pellet burning had proceeded to its fullest extent. Valves "a" and "b" were then opened and the system vacuum flushed four times with air to remove the helium. The system was then evacuated to approximately 500 microns and the measurements of the quantity of unreacted magnesium made in the same manner as in the magnesium mass fraction determination.

## DATA AND RESULTS

The determination and method of application of the air and hydrogen solubility corrections are contained in Appendices I and II. Appendix III contains the results of the determination of the mass fraction of magnesium in the mixture.

Ignition actually took place at all pressures. The effect of pressure upon the extent to which the reaction proceeded is shown in Figure 4 and all data are listed in Table 1. No effect was observed on the extent of the reaction for pressures above approximately 0.5 atmosphere. Below 0.5 atmosphere a gradual decrease in the extent of the reaction was noted as the pressure decreased to approximately 100mm. At pressures below 100mm the extent of the reaction dropped off rapidly.

While no particular attempt was made to determine the flame temperature, it was apparently somewhere between the melting point of platinum,  $1773^{\circ}\text{C}$ , and the boiling point of platinum,  $4300^{\circ}\text{C}$  /14/. This was evidenced by an examination of the platinum ignition wire after firing. The wire gave definite indications of having melted as a result of the heat generated during the reaction since preliminary test indicated the current was not of sufficient magnitude to melt it within the times involved. However, reweighing indicated no change in mass at all except for one run. At the completion of this run, pressure 296 mm, an eight percent decrease in the weight of the platinum wire was noted. However, a sizeable piece of the wire was observed to be fused to the bomb wall. In addition what appeared to be a small piece of fused magnesium was found remaining in the bomb, the mass of which was 0.61 milligrams. For this reason run number 12 was omitted from the calculations.

TABLE 1

## IGNITION AND BURNING DATA

Run	1	2	3	4	5	6
$V_o$	830.00	830.00	830.00	830.00	830.00	830.00
$T_o$	22.47	22.49	22.45	23.38	21.80	21.64
$P_o$	0.60	0.60	0.60	0.55	0.60	0.60
$P_i$	760.0	760.0	760.3	764.8	764.0	763.3
$V_s$	815.36	816.64	816.48	819.40	819.80	819.22
$V_2$	14.64	13.36	13.52	10.60	10.20	10.78
$T_2$	21.80	22.50	22.57	23.00	22.30	22.88
$P_2$	759.9	760.0	760.0	765.2	763.5	763.0
$M_p$	26.07	18.64	19.10	23.09	15.42	15.59
$M_m$	6.21	4.44	4.55	5.50	3.67	3.71
$M_r$	4.89	3.51	3.62	1.55	1.16	1.26
$E$	21.3	20.9	20.4	71.8	68.4	66.0
$P_i$	12.8	13.0	12.8	102.9	102.5	103.7
Ave $E$		20.9			68.7	
Ave $P_i$		12.9			103.0	

TABLE 1 (con't)

Run	7	8	9	10	11	12*	13
$V_o$	830.00	830.00	830.00	830.00	830.00	830.00	830.00
$T_o$	19.50	23.42	22.28	22.80	22.42	21.42	23.00
$P_o$	0.50	0.50	0.45	0.38	0.45	0.50	0.35
$P_1$	762.9	768.0	764.9	766.9	767.4	767.4	754.9
$V_s$	819.59	819.76	818.70	819.90	820.03	819.98	818.75
$V_2$	10.41	10.24	11.30	10.10	9.97	10.02	11.25
$T_2$	20.10	23.40	22.40	21.68	21.66	22.40	23.20
$P_2$	767.9	768.0	764.9	767.0	767.4	767.4	754.5
$M_p$	20.02	18.92	33.38	26.69	29.36	34.40	38.52
$M_m$	4.77	4.50	7.95	6.35	6.39	8.19	9.17
$M_t$	0.96	0.94	1.98	1.39	1.16	0.85	1.91
$E$	79.9	79.1	75.1	78.1	83.4	89.6	79.2
$P_f$	199.0	198.9	197.3	296.3	297.0	296.1	295.7
Ave $E$		78.0				80.2	
Ave $P_f$		197.9				296.3	

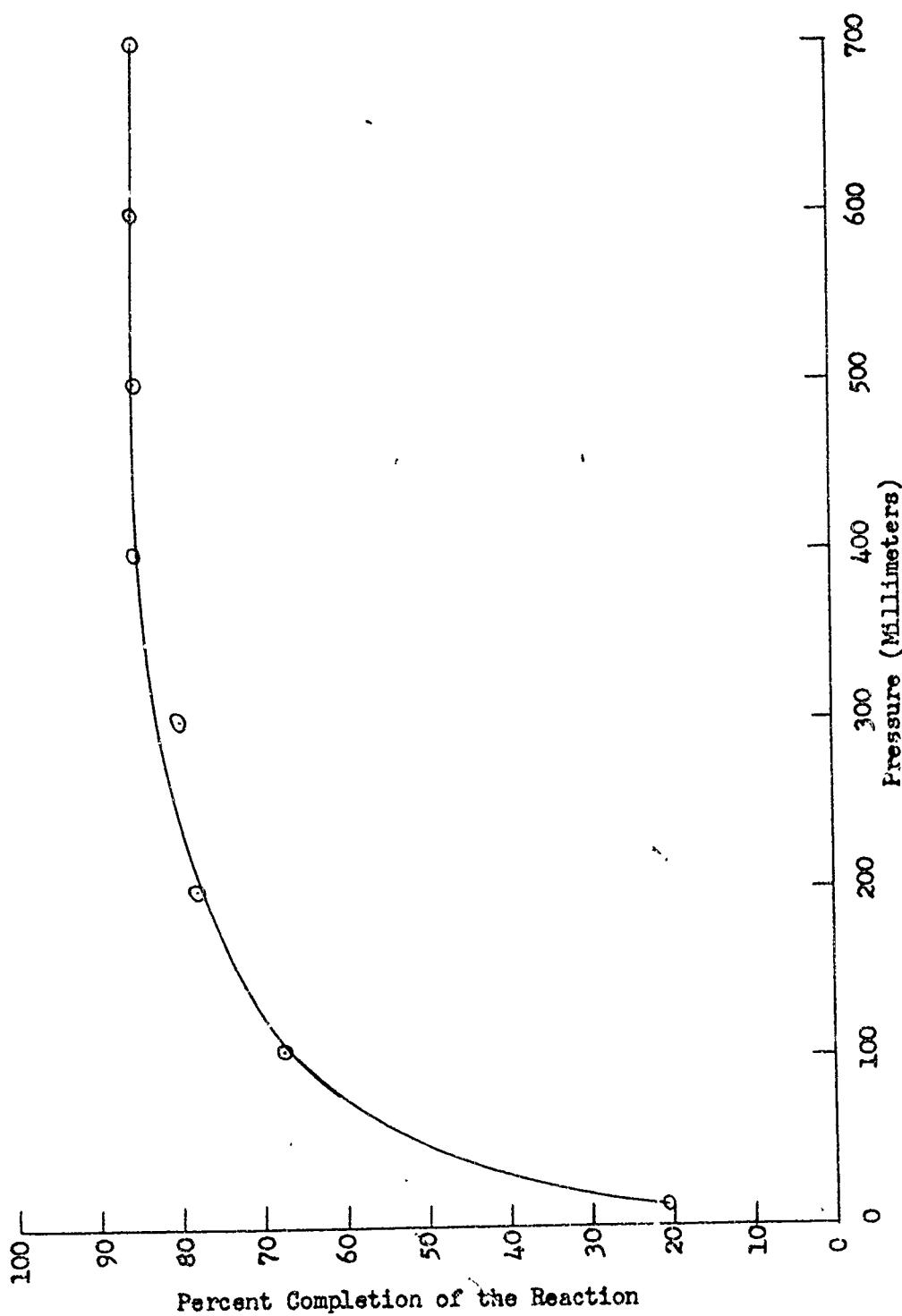
\*Run number 12 was disregarded

TABLE 1 (con't)

Run	14	15	16	17	18	19
$v_o$	830.00	830.00	830.00	830.00	830.00	830.00
$T_o$	23.09	21.94	22.17	23.16	21.93	22.10
$P_o$	0.50	0.50	0.30	0.45	0.40	0.30
$P_i$	766.7	767.2	765.4	765.0	766.3	765.0
$v_s$	818.06	818.61	818.55	819.43	819.02	819.90
$v_2$	11.94	11.39	11.45	10.57	10.98	10.10
$T_2$	22.89	21.80	22.10	22.52	21.82	21.96
$P_2$	766.5	767.4	765.0	764.9	766.2	764.8
$M_p$	58.72	54.63	74.37	35.85	57.24	34.00
$M_m$	13.98	13.01	17.71	8.54	13.63	8.10
$M_r$	2.56	2.03	1.83	1.63	1.78	1.24
$E$	81.7	84.4	89.7	80.9	86.9	84.7
$P_i$	399.1	398.6	397.5	496.6	496.8	498.5
Ave $E$		85.3			85.2	
Ave $P_i$		398.5			497.3	

TABLE 1 (con't)

Run	20	21	22	23	24	25
$V_o$	830.00	830.00	830.00	830.00	830.00	830.00
$T_o$	* 21.62	22.12	22.63	22.63	22.03	21.96
$P_o$	0.50	0.30	0.30	0.50	0.30	0.30
$P_1$	762.9	764.8	764.4	762.5	764.3	764.0
$V_s$	818.88	819.86	819.44	819.24	818.93	819.32
$V_2$	11.12	10.14	10.56	10.76	11.07	10.68
$T_2$	23.32	22.43	22.29	22.88	23.12	22.10
$P_2$	762.8	764.9	764.4	762.6	764.2	763.9
$M_p$	55.10	37.44	44.21	42.58	49.94	43.46
$M_m$	13.11	8.91	10.53	10.13	11.89	10.35
$M_r$	1.97	1.22	1.65	1.60	1.58	1.61
$E$	85.0	86.3	84.3	84.2	86.8	84.3
$P_i$	596.7	596.4	597.9	698.1	698.8	698.7
Ave $E$					85.1	
Ave $P_i$		597.0			698.5	

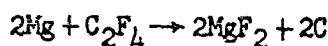


Effect of Pressure on the Extent of the Reaction

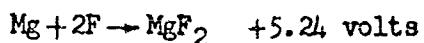
Figure 4

## DISCUSSION AND CONCLUSIONS

Considering the Teflon to be a series of  $C_2F_4$  units, the results of the X-ray diffraction of the products of the reaction indicate that it is reasonable to assume the reaction to be



The presence of the  $MgO$  was assumed to have no effect on the reaction, since the X-ray diffraction patterns made before and after the reaction indicated no appreciable change in the magnesium oxide content. Oxidation potentials listed by Latimer indicate that the formation of the fluoride is favored over the oxide /15/.



In the event that a small amount of magnesium oxide did decompose, the presence of the excess Teflon would thus cause any magnesium resulting from this decomposition to react with fluorine leaving the oxygen to come off as recombined molecular oxygen and possibly a small amount of carbon monoxide. Any carbon monoxide and oxygen thus formed were assumed to be in such dilute concentrations as to have no appreciable effect on the pressure in the bomb or the unreacted magnesium.

From a consideration of the theory of ignition and burning /1/, and the preliminary test conducted on Teflon and the magnesium-Teflon mixture a possible mechanism for the reaction was assumed.

1. The evolving of reactant gases from the Teflon upon heating.
2. The heating of these gases in close proximity to the hot solid surface to a temperature in the vicinity of the melting point of magnesium and concurrent mixing with magnesium vapor.
3. The ignition of the mixed gases followed by steady state burning

when the gases reached the proper temperature.

Since ignition occurred in all instances some of the gases in every case were in the required configuration. At low pressures where burning could not be sustained the reactant gases were either at too low a temperature or were not properly mixed to react. As indicated by Briar, Churchill, and Thacher /4/, there is a definite ignition delay time once ignition or burning temperature is reached in addition to the time for the gases to be heated to the required reaction temperature. Too rapid a diffusion rate of the gases from the hot reaction zone at the solid surface would prevent the gases from reaching the required temperature and composition for reaction. At pressures of approximately 350mm and greater the diffusion rate was maintained at a value low enough to prevent its effecting the reaction. As the pressure was reduced below 350mm, the diffusion rate increased and some of the reactant gases passed out of the reaction zone before reaching the required reaction temperature and composition.

The results obtained should be viewed in the light of a qualitative rather than a quantitative effect of pressure. Consideration should be given to the inaccuracies introduced by the physical make up of the pellets. Since the ignition wire passed through the middle of the pellet, initial ignition took place inside the pellet and burning progressed from the inside out. It is quite possible that at low pressures there was a slight pressure buildup within the pellet which allowed ignition, whereas had ignition been attempted at the outside surface of the pellet it would have been impossible. At the other end of the curve the values of the extent to which the reaction proceeded may be too low. Since the pellets were lightly compressed, it is possible that some of the magnesium was blown away from the reaction zone by the gases generated during the reaction.

before it could react.

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## APPENDIX I

### AIR CORRECTION

A definite quantity of air was introduced into the system with the air saturated acid. Due to the relatively small liquid surface areas, the lack of agitation of the liquid, and the extremely low pressure at the time of introduction of the acid into the bomb, a certain portion of the air was included in the final gas measurement. The amount of air included in the final gas volume is dependent on the solubility of the air in the acid, which in turn is dependent on the partial pressure of the air in the final gas volume /9/.

Zoss, Suciu, and Sibbitt /10/ and Pray, Schweichert, and Minnich /11/ in their investigation of the solubilities of gases in water determined that, for gases whose solubility is small, Henry's Law applies to the dissolved gas over limited pressure ranges. Since all pressures involved here are atmospheric and less, the assumption was made that in addition to Henry's Law, the perfect gas law and Dalton's and Raoult's laws were also applicable.

Solubility values compiled by Seidell /12/ and Loomis /13/ indicate that the solubility of air in aqueous solutions of sulphuric acid of 0.5 normality and less is the same as in water. Since the acid was 0.1 normal it was considered to be pure water for solubility purposes.

For a given volume of gas in the buret the partial pressure and the amount of air can be determined using Dalton's law, the perfect gas law, and Raoult's law since the gas is saturated with water vapor and its temperature is known. The total amount of air in the system can be determined from the evacuated conditions of the bomb and the solubility of air in the acid introduced. Thus the air dissolved in the acid

within the system can be determined.

To determine a relationship between the partial pressure of dry air and the amount of air dissolved in acid at that partial pressure, the partial pressure was normalized, using 760 millimeters as a normalizing factor, and "f", the fraction of the total solubility that the dissolved air represented, was determined (Table 2). The normalized pressure was then plotted against "f" and the equation of the resulting curve determined by the method of least squares (Figure 5).

$$P_n = -74.01f + 44.25 \quad (1)$$

It should be here noted that equation (1) is in no way proposed as a general relationship. Its validity is claimed only for the particular geometry of the system, the conditions existing therein, and over the range of pressures and solubilities involved in the experimental data.

Equation (1) was then used to derive an expression for the partial pressure of air that could be used over the entire range of temperature, pressure and gas volume involved.

$$N_1 = \frac{P_a \Sigma N}{P_2} = N_2 - N_3 \quad (2)$$

$$N_3 = fN_4 \quad (3)$$

By Henry's law

$$N_4 = N_5 \left[ \frac{P_a}{760 - P_3} \right] \quad (4)$$

Substituting (3) and (4) into (2) and rearranging, bearing in mind that

$$P_n = \frac{P_a}{760} \quad \text{yields}$$

$$P_a = \frac{N_2 P_2}{\Sigma N} + \left[ \frac{P_a}{760} - 44.25 \right] \left[ \frac{1}{74.01} \right] \left[ \frac{N_5 P_a}{760 - P_3} \right] \quad (5)$$

collecting terms results in a quadratic in  $P_a$ :

$$P_a^2 - \left[ \frac{(760 - P_3)(5625)(\Sigma N) + (3360)(N_5)(P_2)}{(N_5)(P_2)} \right] P_a + \frac{(760 - P_3)(5625)(N_2)}{N_5} = 0 \quad (6)$$

Equation (6) was then used to solve for the partial pressure of air in the total gas volumes containing water vapor, air, and hydrogen.

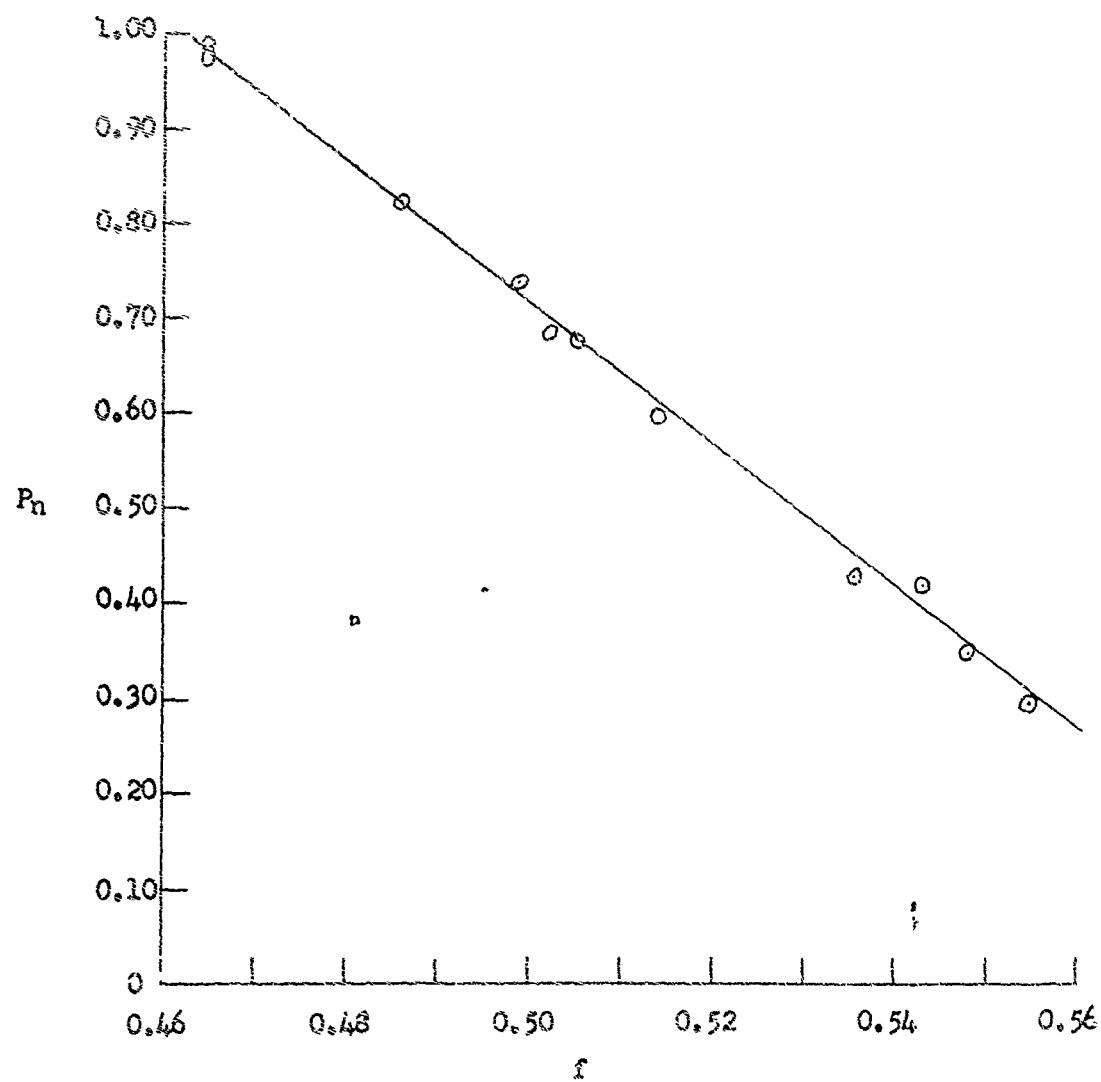
TABLE 2

## AIR CORRECTION DATA

Run	1	2	3	4	5
$V_o$	830.00	882.65	883.00	882.71	884.90
$T_o$	22.54	21.78	22.30	22.61	22.89
$P_o$	0.40	0.40	0.50	0.50	0.50
$P_1$	762.3	770.0	764.3	766.0	766.5
$V_s$	821.72	876.60	875.35	874.76	873.73
$V_2$	8.28	13.67	15.34	15.53	18.00
$P_2$	762.2	582.2	543.9	537.5	483.0
$T_2$	22.52	21.60	22.46	22.60	22.91
$S_1$	0.7184	0.7370	0.7250	0.7220	0.7180
$N_1$	0.3348	0.4196	0.4353	0.4347	0.4508
$N_2$	0.6095	0.6652	0.6583	0.6535	0.6512
$N_3$	0.2747	0.2456	0.2233	0.2208	0.2004
$S_2$	0.7183	0.5608	0.5068	0.5006	0.4454
$P_a$	741.8	562.9	523.5	516.8	462.5
$N_4$	0.5915	0.4915	0.4451	0.4374	0.3896
$f$	0.465	0.499	0.502	0.505	0.514
$P_n$	0.977	0.741	0.688	0.681	0.601

TABLE 2 (con't)

Run	6	7	8	9	10
$V_o$	879.49	860.69	867.47	870.74	830.00
$T_o$	22.87	22.80	22.73	22.56	22.50
$P_o$	0.50	0.40	0.45	0.40	0.35
$P_1$	766.3	763.4	764.2	762.8	766.8
$V_s$	840.30	830.64	844.48	869.38	821.93
$V_2$	42.69	34.16	27.74	11.39	8.07
$P_2$	247.5	288.3	342.6	647.8	766.8
$T_2$	22.90	22.74	22.66	22.63	22.39
$S_1$	0.7162	0.7149	0.7168	0.7181	0.7234
$N_1$	0.5241	0.4591	0.4841	0.3873	0.3271
$N_2$	0.6257	0.6125	0.6266	0.6432	0.6104
$N_3$	0.1016	0.1174	0.1425	0.2559	0.2833
$S_2$	0.2176	0.2579	0.3110	0.6062	0.7259
$P_a$	226.6	267.6	322.0	627.2	745.4
$N_4$	0.1829	0.2142	0.2626	0.5270	0.5966
$f$	0.555	0.548	0.543	0.486	0.465
$v_n$	0.298	0.352	0.424	0.825	0.983



Fraction of Dissolved Air as a Function of the  
Partial Pressure of Dry Air

Figure 5

## APPENDIX II

### HYDROGEN SOLUBILITY CORRECTION

Once the number of moles of hydrogen in the total gas volume was determined it was necessary to apply a correction for hydrogen dissolved in the acid. A series of tests was made in which a known mass of magnesium was reacted with acid in the bomb and the volume of evolved gases measured. Using the same assumptions as in Appendix I along the equation (6) of Appendix I, the partial pressure of hydrogen, the amount of undissolved hydrogen, and the amount of dissolved hydrogen were determined (Table 3). To determine a relationship between the partial pressure of hydrogen in the total gas volume and the amount of dissolved hydrogen at that pressure,  $\log B$ , the log of the ratio of the concentration of dissolved hydrogen to the concentration of undissolved hydrogen was plotted against  $\log P_m$ , the normalized partial pressure of hydrogen (Figure 6). The normalizing factor used was 760 millimeters. Since at  $P_m = 0$ ,  $B = 0$ , the relation was assumed to be of the form;

$$P_m = AB^n$$

The log plot was solved for slope and intercept by the method of least squares resulting in the relation;

$$P_m = 3.564B^{.3453} \quad (1)$$

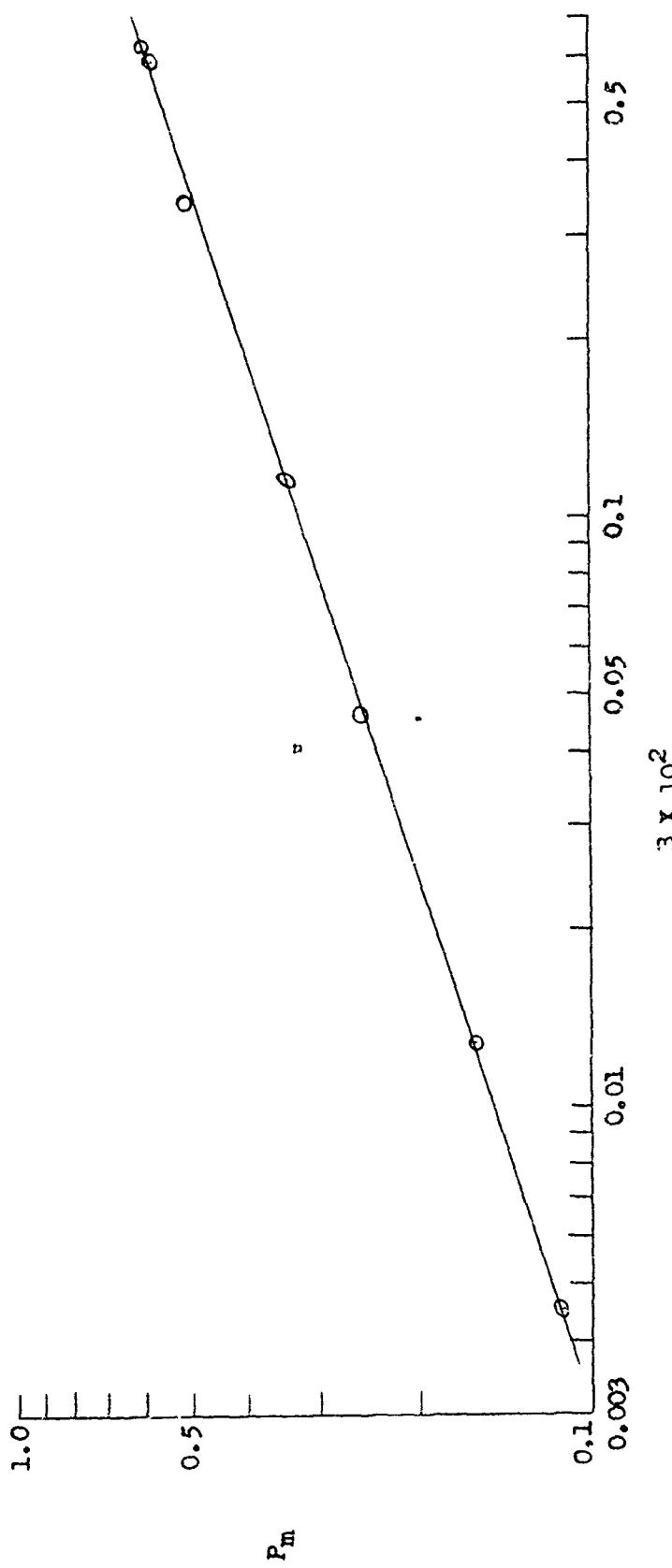
This relationship is proposed as being applicable only to the particular conditions under which the experimental data were obtained. Equation (1) was then used to solve for the amount of dissolved hydrogen during the actual ignition and burning tests.

TABLE 3  
HYDROGEN SOLUBILITY DATA

Run	1	2	3	4	5	6	7
$V_o$	830.00	830.00	830.00	830.00	830.00	830.00	830.00
$T_o$	22.89	22.20	22.83	22.67	22.69	22.80	21.76
$P_o$	0.60	0.50	0.40	0.40	0.45	0.40	0.50
$P_1$	767.8	769.1	761.4	761.3	761.6	764.9	763.9
$V_s$	800.94	795.01	806.53	814.36	816.89	819.15	819.30
$V_2$	29.06	34.99	23.47	15.64	13.11	10.85	10.20
$P_2$	767.8	769.1	761.1	761.2	761.2	765.0	763.4
$T_2$	22.91	22.21	22.64	22.86	22.76	22.72	22.31
$S_1$	0.7280	0.7303	0.7133	0.7149	0.7178	0.7163	0.7185
$N_2$	0.6099	0.6031	0.5933	0.6002	0.6052	0.6048	0.6161
$\Sigma N$	1.209	1.461	0.9680	0.6444	0.5408	0.4499	0.4228
$N_5$	0.5715	0.5736	0.5759	0.5784	0.5845	0.5839	0.5896
$P_a$	305.0	259.4	351.5	480.9	548.0	621.8	657.6
$P_h$	441.8	469.6	389.0	259.4	192.4	122.5	85.6

TABLE 3 (cont.)

Run	1	2	3	4	5	6	7
$N_6$	0.6965	0.9300	0.4947	0.2197	0.1367	0.0720	0.0475
$C_g$ ( $\times 10^2$ )	2.395	2.658	2.108	1.405	1.043	0.6636	0.4674
$M_m$	19.65	25.69	13.43	5.66	3.42	1.77	1.16
$N_7$	0.8080	1.056	0.5522	0.2327	0.1405	0.0728	0.0477
$N_8$	0.1115	0.1260	0.0575	0.0130	0.0039	0.0008	0.0002
$C_1$ ( $\times 10^4$ )	1.392	1.589	0.713	0.160	0.0477	0.0089	0.0021
$B$ ( $\times 10^2$ )	0.581	0.598	0.338	0.114	0.0457	0.0128	0.0045
$P_m$	0.581	0.618	0.512	0.340	0.253	0.161	0.113



Hydrogen Solubility as a Function of the  
Partial Pressure of Dry Hydrogen

Figure 6

### APPENDIX III

#### DETERMINATION OF THE MASS FRACTION OF MAGNESIUM IN THE MAGNESIUM-TEFLON MIXTURE

A known mass of the magnesium-Teflon mixture was allowed to react with acid within the system and the final volume of evolved gases measured. The mass of magnesium in the total mass of the mixture was determined by the methods of Appendices I and II. The resulting mass fractions are listed in Table 4. The average mass fraction used was 1/4.20.

TABLE 4  
MAGNESIUM MASS FRACTION DATA

Run	1	2	3	4	5
$v_o$	830.00	830.00	830.00	830.00	830.00
$T_o$	22.51	22.31	22.89	22.98	22.30
$P_o$	0.30	0.50	0.60	0.60	0.60
$P_1$	762.9	759.9	766.7	765.7	770.8
$v_s$	812.94	813.83	812.93	815.71	805.98
$v_2$	17.06	16.17	17.07	14.29	24.02
$P_2$	763.0	759.7	766.6	765.8	771.0
$T_2$	22.50	22.32	22.87	23.00	22.30
$s_1$	0.7191	0.7190	0.7165	0.7136	0.7294
$N_2$	0.5981	0.6076	0.6095	0.6090	0.6149
$\Sigma N$	0.7061	0.6668	0.7089	0.5926	1.005
$N_5$	0.5822	0.5853	0.5773	0.5775	0.5802
$P_a$	448.8	472.7	459.0	421.2	357.1
$P_h$	293.8	266.8	286.7	223.5	394.0
$N_6$	0.2719	0.2342	0.2651	0.7730	0.5136
$c_g (x 10^2)$	1.594	1.448	1.553	1.211	2.138
$P_m$	0.387	0.351	0.377	0.294	0.518
$B (x 10^2)$	0.1608	0.1216	0.1498	0.0728	0.3761
$c_1 (x 10^4)$	0.2562	0.1762	0.2356	0.0881	0.8041
$N_8$	0.0201	0.0143	0.0189	0.0072	0.0643
$N_7$	0.2916	0.2485	0.2640	0.1802	0.5704
$M_m$	7.10	6.04	6.91	4.38	14.07
$M_p$	29.81	25.48	29.26	18.26	58.95
$r$	1/4.20	1/4.22	1/4.23	1/4.17	1/4.19